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International BureauEx. 6C Fee \$  
X  
Ex. 6C + 7  
Table 5

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

<b>(51) International Patent Classification <sup>5</sup> :</b> <b>C11D 3/37, 17/00, B01D 19/04</b>	<b>A1</b>	<b>(11) International Publication Number:</b> <b>WO 93/01269</b> <b>(43) International Publication Date:</b> 21 January 1993 (21.01.93)
<b>(21) International Application Number:</b> PCT/GB92/01188 <b>(22) International Filing Date:</b> 1 July 1992 (01.07.92) <b>(30) Priority data:</b> 9114195.2 1 July 1991 (01.07.91) GB <b>(71) Applicant (for AU CA GB only):</b> UNILEVER PLC [GB/GB]; Unilever House, Blackfriars, London EC4 4BQ (GB). <b>(71) Applicant (for all designated States except AU CA GB US):</b> UNILEVER NV [NL/NL]; Burgemeester s'Jacobplein 1, NL-3015 CA Rotterdam (NL). <b>(72) Inventors; and</b> <b>(75) Inventors/Applicants (for US only):</b> AKAY, Galip [TR/GB]; Elaskan, Moorcroft Close, Sidmouth, Devon EX10 8SU (GB). GARRETT, Peter, Robert [GB/GB]; Charlesville, Cilcain Road, Pantymwyn, Mold, Clwyd, Wales CH7 5NL (GB). YORKE, John, William, Harold [GB/GB]; 1 Stonebank Drive, Little Neston, South Wirral L64 4DL (GB).		<b>(74) Agent:</b> FORD, Michael, F.; Mewburn Ellis, 2 Cursitor Street, London EC4A 1BQ (GB). <b>(81) Designated States:</b> AU, BR, CA, US, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IT, LU, MC, NL, SE). <b>Published</b> <i>With international search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>  Ex. 6C 17 → 102 Table 5 claim 1, 2, 3, 5, 6, 7, 9, 11, 12
<b>(54) Title:</b> ANTIFOAM INGREDIENT  <b>(57) Abstract</b>  Antifoam particles for incorporation into a particulate detergent product comprise a high viscosity silicone antifoam absorbed onto a porous, particulate organic carrier exemplified by cellulose or wood flour. This avoids deactivation which occurs when this kind of antifoam is absorbed on an inorganic carrier. The organic carrier and antifoam are enclosed by a coating layer.  102 - 4, 11 - 11, 7 8 - not pub.		

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ANTIFOAM INGREDIENT

This invention relates to antifoam particles with silicone as the antifoam active material.

5

It is well known to incorporate into detergent products a material which will reduce the formation of foam. This is done to avoid the production of excessive, i.e. inconveniently large, amounts of foam particularly in countries where front loading washing machines are commonplace.

It is well known that silicone oils, possibly mixed with finely divided silica, are effective at reducing foaming. Silicone oils which are frequently used have a viscosity of about 3,000 centipoise. The silicone oil is absorbed onto a porous carrier in order to place it in a particulate form. Typically sodium carbonate, sodium perborate or sodium tripolyphosphate is used as a carrier substance.

It is also known that higher molecular weight silicone oils, notably oils with a viscosity of at least 10 Pa.sec (10,000 centipoise) are more effective antifoam agents if an equal weight of silicone oil is used. However we have found that there is an obstacle to use of these materials. If they are absorbed on to the inorganic carrier substances

which are conventionally used with lower molecular weight silicone oils, they lose their activity.

EP-A-142910 discloses a blend of silicones, having a high overall viscosity, dispersed in a water-soluble or water-dispersible organic carrier which has a melting point not exceeding 90°C. We have found that it is very difficult to obtain stable dispersions of high viscosity silicone in a molten organic carrier, and consequently it is difficult to obtain solidified dispersions of the kind contemplated by this prior document.

Unexpectedly, we have now found that the loss of activity of absorbed high viscosity silicone oil can be avoided by use of certain particulate, solid organic carrier materials and by coating the resulting particles. This also avoids the need to disperse high viscosity silicone in a melt of organic carrier.

Therefore, according to this invention, we provide antifoam particles for incorporation into a detergent product comprising a porous particulate organic carrier material;

silicone antifoam with a viscosity of 10,000 cP or more absorbed onto the porous carrier; and

a coating layer enclosing the carrier and absorbed silicone antifoam.

The organic carrier material may be a finely divided solid with inter-particle rather than intra-particle porosity.

5           A number of useful organic carrier materials have a Hildebrand solubility parameter of at least 24 MPa<sup>1/2</sup>, and such materials may be preferred.

Hildebrand Solubility Parameters are discussed in  
10 various textbooks, including:

J H Hildebrand and R L Scott, "The Solubility of Non-electrolytes" Reinhold 1950, in "Encyclopedia of Polymer Science and Technology", Wiley, 1965 "Polymer Handbook" 3rd edition edited Brandrup and Immergut, Wiley 1989.

15           A number of values are given in the last mentioned reference.

The organic carrier material will generally not have a melting point below 100°C and it may or may not be water-  
20 insoluble.

The materials which may be used in this invention and other preferred features will now be discussed in greater detail.

25

#### The silicone antifoam

This is silicone oil having a dynamic viscosity of at least 10,000 centipoise. The viscosity may be well above

this figure, for instance in the range 20,000 to 30,000 centipoise. Viscosity is sometimes quoted as kinematic viscosity, in centistokes. The latter is the dynamic viscosity divided by the density.

5

The silicone oil may have silica particles suspended therein as antifoam promoter, as is conventional for silicone antifoams of lower viscosity.

10        Suitable silicone oils are available from Dow Corning, notably Dow-Corning X2-3302.

The organic carrier

15        The organic carrier material must be porous, and hence  
able to absorb silicone oil. This porosity may be inter-particle rather than intra-particle.

A number of suitable organic carriers are polymeric in nature and have a molecular weight in excess of 1,000.

20

The preferred feature of a solubility parameter of 24 MPa or more signifies that the carrier material should be relatively highly polar in nature. Such organic carrier materials often have water associated with their structure.  
25 They include glucose, cellulosic and proteinaceous materials as well as polyvinyl alcohol. In particular, fibrillated cellulosic materials can display high absorbence for silicone oil, extending up to as much as 2.5 times the

weight of cellulosic material. Commercially available cellulosic materials include wood flour, hydrolysed cereal solids, jute and cotton flock. Preferred materials include glucose, sucrose and polymers incorporating glucose residues  
5 such as cellulose.

Wood flour and fibrillated cellulose are examples of materials whose particles have large aspect ratio, large inter-particle porosity but low intra-particle porosity.  
10

It is desirable that the carrier material does not melt below 100°C. Then it does not melt during the washing process. It may have no melting point at all, as for instance in the case of cellulose which does not melt but  
15 eventually decomposes when heated sufficiently.

Polymeric carrier materials may have a molecular weight substantially above 1,000, e.g. greater than 2,000.

20 As will be shown by examples below, when high viscosity silicone antifoam is absorbed onto an unsuitable carrier material activity is lost even when the resulting composition is stored out of contact with other materials. By contrast, when the oil is absorbed onto a suitable  
25 carrier material, the compositions can be stored for some weeks without loss of antifoam activity. Consequently the suitability of a possible carrier material can be tested by

absorbing high viscosity silicone antifoam on it, storing and then testing the antifoam activity.

#### Surrounding coating

5           We have observed that when a high viscosity antifoam is absorbed on a suitable carrier material, so as to have good storage life in isolation, the antifoam activity is lost on contact with detergent powder. We have found though that this difficulty can be overcome by coating the particles of  
10 carrier material with absorbed silicone antifoam so that the coating inhibits escape of antifoam from the carrier particles and hence blocks contact between the antifoam and the detergent powder during storage of the detergent composition.

15

A coating may also delay release at the time of use.  
Materials which may be used to provide coating layers include organic polymers and polymer blends, non-soap  
surfactants which may possibly be derived from a polymer  
20 such as fatty acyl and diacyl derivatives of polyethylene glycol, and mixtures of soap with fatty acid.

Suitably, the coating is an impervious layer (unlike the porous carrier). However, it will be appreciated that a  
25 coating which is effective to retain a large majority of the antifoam within the coated particles during storage can be effective to retain a large proportion of the activity of the silicone antifoam, even though a small proportion of



silicone antifoam may escape through the coating and become deactivated. A second coating may be applied over the top of a first coating so as to create a more effective barrier to the escape of silicone from the particles.

5

In order to assist the release of the silicone antifoam from the particles at the time of use, the material which is encapsulated by the coating, or material which is embedded within the coating may include a constituent which will  
10 swell or effervesce in contact with the water of a wash liquor so that initial penetration of water will cause swelling which in turn will cause outright rupture of the coated particles. An effervescent material which will cause swelling by liberation of gas may be an acid which can react  
15 with carbonate or bicarbonate present in the wash liquor or it may be both particles of an acid and particles of carbonate or bicarbonate. These will not react as long as they are dry but will react together causing effervescence once they are wetted by wash water.

20

When two coatings are provided, one useful possibility is that the inner coating provides mechanical strength while the outer coating provides a barrier to prevent escape of the antifoam. Another possibility is for the outer coating  
25 to be a water-insoluble or poorly soluble. Such an arrangement can serve to delay release of the encapsulated material when the particles are placed in water until such time as the water has penetrated the outer coating (and

then, more rapidly, the inner coating). Swelling of the inner particles when water does penetrate to them may at that point serve to rupture the outer coating so that after a delay caused by the outer coating the subsequent release is not restrained by the outer coating. The release of the water insoluble outer coat can also be achieved when its temperature is raised above its melting temperature during wash.

10 We have found that the escape of traces of high viscosity silicone antifoam, in quantities which are too small to be detrimental to storage stability, can have a detrimental effect on the ability of the powder to dispense from the dispenser drawer of an automatic washing machine during use.

We found, however, that this undesirable effect can be counteracted by including effervescent material in the coating. When dispensing of powder from a dispenser drawer of a washing machine is a significant consideration, as is the case in Europe, it is a preferred feature of this invention to incorporate such effervescent material in the coating.

25 Effervescent material can be an acid and a carbonate which will not react in the coating, or can be solely an acid, to react with a carbonate-containing wash liquor.

Examples of coating materials which may be used alone or in blends are:

1. Polyethylene glycol (PEG) and polyethylene oxide  
5 (PEO): This system provides a very extensive range of molecular weight ranging from several hundreds to several millions. PEGs can be used by themselves as coating agent or may be used to dissolve other polymers.
  2. Polyvinyl pyrrolidone (PVP): Generally used in  
10 combination with other polymers.
  3. Poly (acrylic acid) (PAA): Weak acid. Of use in systems where release of the coated material is dependent on pH.
  4. poly (caprolactone) (PCL); poly (caprolactone) diol,  
15 (PCL-diol).
- PCL has high permeability despite the fact it is not water soluble. May also be used to form blends with other water soluble polymers. It is also biodegradable.
5. Poly (ethylene-vinyl acetate)  
20 copolymer (EVAC-CP).
  6. Poly (ethylene-acrylic acid)  
copolymer (EAA-CP).
  7. Oxidised polyethylene (OPE): This polymer is used to provide compatibility between polyalkylenes and water-  
25 soluble polymers or to modify the release characteristics of the other water-soluble polymers such as PEG's and PEO's.
  8. Polyethylene glycol - fatty acid esters: These polymeric surfactants offer a wide range of melting point

and water solubility/dispersibility depending on the length of the polyethylene glycol chain and fatty acid chain. For example the monolaurate of polyethylene glycol with average molecular weight 6000 has melting point of 61°C and is highly water-soluble while the dilaurate of polyethylene glycol with average molecular weight 600 has melting point of 24°C and is not water-soluble, merely water-dispersible. These materials can be used to provide two coatings which are compatible with each other but have different properties. PEG 6000 monolaurate can be used to provide a mechanically strong water-soluble first coating while PEG 600 dilaurate can be applied as a second coating forming a vapour barrier.

Blends of materials which have been found useful are:

1. Soap/fatty acid/polymer, especially sodium stearate/lauric acid/ethylene acrylic acid copolymer with a weight ratio 0.5 to 2.0 : 0.5 to 2.0: 1. Here, the presence of the polymer can lead to a lowering of melting point, crystallinity and crystal size. It also modifies the water solubility of the coating.
2. Fatty alcohol ethoxylate/polymer especially when the polymer is in lesser amount than the fatty alcohol ethoxylate and is polycaprolactone or ethylene acrylic acid copolymer.

Inclusion of such polymer or other polymers leads to an increase in melting point and in the hardness of the coating material.

- 5     3.     Polyethylene glycol/citric acid.     Anhydrous citric acid can be dissolved in PEG at temperatures of about 70°C or above.     If the PEG has a molecular weight greater than 4,000, a mechanically strong, weakly-crystalline solid material is formed upon cooling.     Such a blend may be used  
10     as an outer coating.     The weight ratio of PEG to citric acid would typically lie in a range from 3:1 to 1.5:1.

Such a blend of PEG and citric acid is preferably formed using PEG of molecular weight 6,000 - 12,000.

- 15     A blend of PEG and citric acid may also incorporate particles of other materials such as silica, a carbonate or a bicarbonate which will react with the citric acid in the presence of water at the time of use.

20     Method of production

Absorption of the silicone antifoam onto the carrier material can be accomplished merely by mixing the materials together, for example using a Z-blade mixer.

- 25     Coating of carrier material particles with absorbed antifoam can be carried out using various known coating techniques.     It can be sufficient to bring about agglomeration, using a binding agent which then forms a

coating. The preferred method, however, is the process described and claimed in our published European application  
→ EP-A-382 464 the disclosure of which is incorporated herein by reference.

5

The process set out in that European application comprises a first step of forming a melt of a coating material with a disperse phase therein,

and a second step of destabilizing the melt by  
10 addition of solid particles and/or by cooling, causing the melt to crumble to a particulate form whereof the particles comprise the coating material with the disperse phase embedded therein. For application of that process to the present invention, the particles of carrier material with  
15 absorbed antifoam constitute the said disperse phase.

Solid particles which are added to induce crumbling are conveniently referred to as a "crumbling agent".

20 When carrying out this coating process it is desirable to avoid severe stresses which could cause break up of the porous organic carrier. Low rotational speed of any mixer is therefore preferable. It may be desirable to dose the molten coating material onto the organic carrier with  
25 absorbed antifoam until melt formation commences, then start cooling and the addition of crumbling agent without waiting for complete formation of a molten mess.

Addition of crumbling agent preferably takes place with the temperature of the melt only slightly above the melting point of the coating material: 5°C above the melting point is suitable. Desirably the addition of  
5 crumbling agent is accompanied by cooling of the mixture.

It has been found convenient to add around 65% of the crumbling agent while holding the temperature just above the melting point of the polymeric material and then start  
10 cooling while adding the balance of the crumbling agent. Crumbling of the melt will generally commence before all of the crumbling agent has been added but the further addition of crumbling agent will complete the process and may bring about some further crumbling to smaller sized particles. It  
15 is desirable to continue mixing until the temperature has cooled to 30°C less than the melting point of the coating material.

The process can be carried out as a batch process, for  
20 instance using a Z blade mixer, or as a continuous process, for instance using a twin screw-extruder with more than one zone for introduction of material into the extruder. In a batch process, crumbling could be brought about in different apparatus from that used for initial melt formation.

25

When a coating includes solid, as in the case of a PEG/citric acid blend, some more of the same solid can be used as the crumbling agent.

Overall detergent product

Antifoam particles in accordance with the present invention will normally be admixed into a detergent product. This will generally be a particulate product including detergent active and detergency builder. A detergent product will typically contain 5 to 40% of detergent active and 10 to 70% of detergency builder, by weight based on the whole product. Other conventional materials typically present in such products include some or all of bleach, bleach activator, antiredeposition agents, fluorescer and filler.

Antifoam particles in accordance with this invention may contain carrier material and silicone antifoam in a weight ratio ranging from 4:1 to 1:3. The silicone antifoam may constitute from 3 to 40% by weight of the coated antifoam particles more usually from 5 to 30% by weight.

Antifoam particles in accordance with this invention will typically provide 0.1 to 10% by weight of a detergent product more preferably 0.2 to 5% by weight, yet more preferably 0.05 to 3% by weight of the detergent product.

The quantity of antifoam particles incorporated in a detergent product will generally be arranged such that the content of silicone antifoam based on the overall detergent



product ranges from 0.05 to 3% by weight of the overall detergent product.

Examples of the invention are set out below.

5 Percentages and amounts are by weight unless otherwise stated.

A number of materials are referred to by trade names or abbreviations. A key to these is as follows:-

10

X2-3302: High viscosity silicone antifoam, viscosity 30,000 cS, ex Dow Corning.

15

Avicel PH 101: Porous microcrystalline cellulose (ex FMC Corporation). Particle size = 50  $\mu\text{m}$ , total intrusion volume = 2.15  $\text{cm}^3/\text{gram}$ .

Avicel PH 105: As above but particle size = 20 $\mu\text{m}$ .

20

SCMC: Sodium carboxymethyl cellulose, mol.wt 250000 ex BDH. It is used with Avicel PH 101 after the absorption of silicone antifoam into Avicel PH 101.

25

Avicel WC 595 Co-dried blend of sweet whey (75%), microcrystalline cellulose (22%) and sodium carboxymethyl cellulose (3%). Main ingredients of whey are lactose (65%) and protein (12%).

Elcema P050 Cellulosic powder, ex Degussa, particle size 1-50 $\mu\text{m}$ .

- Elcema F150 Fibrillated cellulose, ex Degussa,  
particle size 1-150µm.
- 5 PEG 6000 DS: Polyethylene glycol (molecular weight =  
6000) distearate. Melting point = 55°C,  
hydrophile-lipophile balance = 18.4  
(water soluble); ex Courtaulds  
Chemicals.
- 10 PEG 200 DS: Polyethylene glycol (molecular weight =  
200) distearate. Melting point = 34°C;  
hydrophile-lipophile balance = 5.0  
(dispersible not soluble in water); ex  
Courtaulds Chemicals.
- 15 PEG: Polyethylene glycol - number following  
PEG indicates molecular weight (Mw), ex  
Fluka AG.
- AC5120: Ethylene - acrylic acid copolymer, Mw =  
3500, Acid number - 120mg KOH/g; ex  
Allied-Signal.
- 20 Aerosil R972: Pyrogenic hydrophobed silica (ex  
Degussa), particle size 16nm.

Example 1

High viscosity silicone antifoam (Dow-Corning X2-3302) was mixed with various carrier materials in a sufficient amount that the silicone constituted about 25% by weight of the resulting compositions. These antifoam compositions were stored for various periods of time. Then the antifoam activity of each composition was assessed. Assessment was carried out using 200g of a detergent powder whose formulation is given in Table 1 below. This was used to wash a clean cotton load (2.5kg) in 16 litres of 12° French hardness water using a front-loading automatic washing machine. At the start of the wash sufficient amount of antifoam granules was added to the detergent base powder to obtain silicone antifoam level of 0.5 wt%. The composition of the detergent base powder used in the foaming tests is given in Table 1. After 45 minutes the height of the foam in the washing machine was noted on a scale from 0 to 100 marked on the machine. The results obtained are set out in Table 2 below.

TABLE 1

<u>Spray dried materials.</u>		% by weight
5	Sodium C <sub>12</sub> -C <sub>13</sub> alkyl benzene sulphonate	9
	C <sub>12</sub> -C <sub>13</sub> alcohol 7EO	1
	Zeolite	24
	Sodium polyacrylate	3
	Sodium carboxymethyl cellulose	0.5
10	Sodium carbonate	2
	Water and minors	11.5
		----
		51
15	<u>Subsequently added materials.</u>	
	Sodium sulphate/sodium carbonate double salt	16
	C <sub>12</sub> -C <sub>13</sub> alcohol 4EO carried thereon	4
	Sodium perborate monohydrate	29

20

Table 1. Composition of detergent base powder used in foam control tests described in Example 1.

TABLE 2

Carrier Material	Solubility Parameter (MPa <sup>1/2</sup> )	Mean Particle size (µm)	Storage Period (Weeks)	Inter Particle Porosity	Intra Particle Porosity	Total Porosity	Foam Height after 45 minutes
Sodium carbonate		120	1	0.84	0.28	1.14	100
Sodium bicarbonate		80	1	0.36		0.36	100
Hydrated alumina			4	3.23		3.23	100
Sodium chloride		32	2				100
Avicel PH 101	32.0	50	1	1.97	0.18	2.15	1
Avicel WC 595	42.8	--	1	0.87	0.13	1.00	1
Polyvinylpyrrolidone (crosslinked)	21.1	180	5	2.93		2.93	43
Polyvinyl alcohol Mol wt 2,000	25.8	350	7				10
Polyvinyl alcohol Mol wt 20,000	25.8	700	5	0.69		0.69	2
Gelatin	26.8	330	8	0.77		0.77	2
Urea	32.3	540	5				55
Wood flour	32.0	340	2	4.23		4.23	9
Polyethylene	16.2	270	2				32

It can be seen from this Table that to a varying extent, antifoam activity was retained during storage when the carrier was an organic material. In particular Avicel  
5 PH 101, polyvinyl alcohol, gelatin, and wood flour all gave low foam heights. All of these materials are organic, generally polymeric in nature, and with a solubility parameter exceeding 24.0 MPa<sup>1/2</sup>.

Example 2

The procedure of Example 1 was repeated using several organic materials, with various loadings of high viscosity silicone on the carrier, and a storage period of 1 week in every case. These loadings all fell within a range of 10 to 50% by weight. The materials and the results obtained are set out below.

	Carrier Material	Solubility Parameter (MPa <sup>1/2</sup> )	Antifoam Loading	Foam Height after 45 minutes
10	Starch	<30	28%	6
15	Cellulose	32.2	40%	5
	Hydroxyethyl	<24	40%	17
20	Sodium carboxy methyl cellulose	<30	20%	21
	D-Glucose	-	15%	12

Example 3

Antifoam particles, without coating, were prepared by mixing equal amounts of Avicel PH 101 microcrystalline cellulose and X2-3302 silicone antifoam in a Z-blade mixer, at approximately 60°C. The antifoam was absorbed by the cellulose and a powdery material resulted. The resultant powder is kept at 60°C under vacuum for 24 hours before being used or stored under ambient conditions.

Some of this material was agglomerated in the same mixer into larger particles by mixing with a small amount of sodium carboxymethylcellulose (SCMC) and water. The resulting particles were of composition (% by weight on dry basis)

15

Avicel PH 101	57%
Antifoam	38%
SCMC	5%.

20

Avicel PH 101 contains residual water not exceeding 5 wt%.

The foam control profile of these particles was assessed in a manner similar to the previous example. The particles were mixed into the washing powder set out in Table 1 in sufficient quantity to provide 0.5 wt% antifoam in the powder. During the wash period the height of foam is observed at intervals.



The foam control profile was assessed in this way for particles stored for one week before mixing with washing powder and particles stored for eight weeks before mixing into washing powder and testing. The results showed very little difference, signifying storage stability. The results were:

	15 mins	Foam height during wash		
		30 mins	45 mins	60 mins
after 1 week :	0	0	0	10
after 8 weeks:	0	2	6	10.

#### 15 Example 4

Example 3 was repeated using Avicel WC595. The anti-foam particles contained 60% of Avicel WC595 and 40% of X2-3302 silicone anti-foam. Avicel 595 contains residual water in an amount not exceeding 5 wt%. Foam control profiles were assessed after storage for one week and after storage for eleven weeks. The results were:

	15 mins	Foam height during wash		
		30 mins	45 mins	60 mins
after 1 week :	0	0	1	6
after 11 weeks:	0	3	8	25.

Example 5

Antifoam particles were produced as in Example 1 and then coated with various coating materials. The coating procedure was in accordance with EP-A-382 464. It was as follows:

The antifoam particles were placed in a Z-blade mixer at a temperature of about 80°C. The coating material was melted separately and added progressively to the Z-blade mixer at a temperature of 70-80°C which was above its melting point. A dispersion in the coating material began to form. The mixer was cooled to 55-60°C and a powdered solid was added to induce crumbling. Cooling of the mixer continued. Mixing was continued until the temperature had fallen to 30-40°C.

In some cases a second coating of PEG 1500 was applied by a similar procedure but with a maximum temperature of 50-55°C. A comparative experiment utilised particles without any coating.

In each instance the final product obtained had the appearance of a dry particulate solid.

Coated particles prepared in this way contained materials as set out in Table 4 below where all percentages are by weight based on the final particles. Particles with

no coating were included as a comparison and appear as Example 5A in Table 4.

These various particles were tested in a detergent  
5 powder whose formulation is given in the following Table 3.

TABLE 3

Composition of detergent base powder used in the  
5 dispensing tests.

	<u>Component</u>	<u>wt %</u>
	Sodium C <sub>12</sub> -C <sub>13</sub> alkylbenzene sulphonate	11.75
	C <sub>12</sub> -C <sub>13</sub> alcohol 7EO	3.52
10	Copolymer of maleic anhydride and acrylic acid	6.38
	Sodium carboxymethyl cellulose	0.72
	Zeolite	33.13
	Sodium carbonate	7.84
15	Water	14.21
	Minors	1.22
	<u>Then add</u>	
	Wax	0.60
20	C <sub>12</sub> -C <sub>13</sub> alcohol 3EO	5.98
	Zeolite	6.39
	Sodium carbonate	4.26
	Fatty acid	2.30
	Water	1.70
25		-----
	Total	100.00

Bulk density is greater than 850 kg/m<sup>3</sup>.

Samples of the various antifoam particles were mixed into samples of the above powder using a mechanical (Turbula) mixer for 15 minutes. The amount of the particles was sufficient to give a silicone oil content of 0.6% by weight. The resulting mixtures were stored for four weeks at 37°C in sealed glass jars and then the antifoam activity was tested by the procedure given in Example 1. Foam heights after 45 and 60 minutes are given in Table 4.

These show that application of a coating as in Example 5B and 5D enhanced the storage stability of the antifoam, and a second coating gave a greater improvement.

The dispensing of these samples from a washing machine was tested using a dispenser drawer as fitted to a Phillips (trademark) AWB126 washing machine. A 100g dose of powder is placed in the main compartment of the drawer and tap water at 10°C and 12° French hardness is allowed to flow through at a rate of 5 litre/min for two minutes. At the end of this period the flow is stopped, excess water is poured off, the residual mass is dried in an oven at 60°C for 8 hours and subsequently weighed. This weight of dispenser residue is expressed as a percentage of the dry powder initially placed in the dispenser drawer. The test was carried out four times and the results are included in Table 4.

The results show that the presence of citric acid in the coating, which effervesces with carbonate from the detergent powder when wetted during dispensing, is  
5 beneficial in reducing residue left in the dispenser.

TABLE 4

		wt% of overall particles					
5	Example No.	5A	5B	5C	5D	5E	5F
	<u>Antifoam and carrier</u>						
	Elcema P050	-	-	-	35.0	18.7	12.5
	Elcema F150	55.0	34.2	23.0	-	-	-
10	X2-3302	45.0	28.0	19.0	23.0	11.0	8.2
	<u>First coating</u>						
	Sodium stearate	-	10.5	7.0	9.0	4.1	3.7
	Lauric acid	-	10.5	7.0	9.0	4.1	3.7
15	AC5120	-	2.3	1.4	2.0	0.9	0.8
	<u>First crumbling agent</u>						
	Citric acid	-	8.7	5.8	17.0	7.1	5.8
	Elcema P050	-	5.8	4.5	5.0	2.1	1.7
20							
	<u>Second coating</u>						
	PEG 1500	-	-	7.0	-	12.0	9.7
	Citric acid	-	-	25.3	-	40.0	53.9
25	Foam height after 45 minutes	43	16	3	9	6	12
	Foam height after 60 minutes	53	20	9	17	9	14
30	Residue	30	21	9.4	8.6	2.2	0

Example 6

Antifoam particles were prepared by mixing X2-3302  
silicone antifoam with Avicel PH 101 microcrystalline  
5 cellulose.

These particles were then coated with various  
materials and the resulting particles were coated again  
with different materials, in a manner generally similar to  
10 the previous Example.

In the first coating stage, the first coating material  
at a temperature  $T_{MAX-1}$  was mixed with the antifoam  
particles (as solid dispersed phase). When melt formation  
15 was observed, the melt was cooled down to a temperature  $T_{C-1}$   
just above the melting point of the first coating material  
and a crumbling agent was added. Cooling was continued  
until a temperature  $T_{MIN}$  was reached. In the second coating  
stage, the temperature of the coated particles from the  
20 first stage was raised to  $T_{MAX-2}$  and the second coating  
material was added at this temperature. Mixing was  
continued until the agglomeration of the particles was  
observed. At this stage the temperature was lowered to a  
temperature  $T_{C-2}$  just above the melting point of the second  
25 coating material and a small amount of crumbling agent was  
found to be sufficient to obtain crumbling. These double  
coated particles were then cooled to ambient temperature  
while continuing to mix.



The materials used, their amounts as percentages by weight based on the final particles and the temperatures conditions observed during coating are set out in the following Table 5.

The antifoam activity of these particles and the dispenser residue from a powder containing them were measured after two weeks of storage at room temperature.

Antifoam activity was tested in the same manner as in Example 1. For this the antifoam particles were incorporated into a detergent powder of the composition set out in Table 1 in a sufficient amount that there was 0.5 wt% silicone antifoam based on the overall powder. Powder dispensing tests were carried out in the same manner as in Example 5. For these tests antifoam granules were mixed into the detergent powder set out in Table 3, in an amount sufficient to provide 0.6 wt% of silicone antifoam based on the overall powder. Mixing was carried out by mechanical mixing (Turbula Mixer) for 15 minutes.

The foam heights after 45 and 60 minutes and the dry dispenser residue as a percentage of initial powder in the dispenser are included in Table 5.

TABLE 5

wt% based on overall particles

Example No.	6A	6B	6C
5	<u>Antifoam on carrier</u>		
	Avicel PH101	37.0	30.0
	X2-3302	21.0	19.0
	<u>First coating</u>		
10	PEG 6000 DS	22.0	-
	Sodium stearate	-	7.5
	Lauric acid	-	7.5
	AC 5120	-	1.0
15	<u>First crumbling agent</u>		
	Aerosil R972	3.0	1.0
	Citric acid	-	-
	Sodium bicarbonate	-	-
	T <sub>MAX-1</sub> (°C)	70	70
20	T <sub>1</sub> (°C)	55	60
	T <sub>MIN</sub> (°C)	37	30
	<u>Second coating</u>		
	PEG 200 DS	15.0	-
25	PEG 1000	-	10.0
	<u>Second crumbling agent</u>		
	Aerosil R972	2.0	-
	Citric acid	-	10.0
	Sodium bicarbonate	-	15.0
	T <sub>MAX-2</sub> (°C)	40	45
	T <sub>2</sub> (°C)	35	40
	Foam height after 45 minutes	-	11
35	Foam height after 60 minutes	-	25
	Dry residue (wt%)	44	37

Example 7

This example describes a triple coating of the high viscosity antifoam with a water insoluble surfactant coat  
5 followed by a water soluble coat which contains an effervescent powder and finally a third outermost water soluble coat which contains a water absorbing layer of anhydrous sodium carbonate. In this process, high viscosity antifoam is absorbed onto microcrystalline cellulose (Avicel  
10 PH 101) and coated with a mixture of sodium stearate, lauric acid and ethylene acrylic acid copolymer (AC5120) (weight ratios 45 : 45 : 10) at 75°C in a 1Kg capacity Z-blade mixer with a rotational speed of 20 rpm. After the addition of the first coating material at 80°C the temperature is  
15 reduced to 55°C when part of the finely ground effervescent powder consisting of 55% anhydrous citric acid and 45% sodium bicarbonate at 25°C is added and the temperature is reduced to 35°C, thus completing the first coating stage.

20 { This product is re-heated to 55°C and coated with PEG 1500 added slowly while the mixing is still continued. The remainder of the effervescent powder is added after reducing the temperature to 50°C. These particles are re-coated at 50°C using more PEG 1500 followed by the addition of anhydrous fine sodium carbonate. The final composition of  
25 these effervescent granules is given below:

		wt%
	Constituents of the coated granules	
	Solid dispersed phase (Avicel PH 101)	14
	Silicone antifoam	7
5	First coat (sodium stearate + lauric acid + ethylene acrylic acid copolymer AC 5120; wt.ratios 45 : 45 : 10)	6
10	Effervescent crumbling agent for the first coat (citric acid + sodium bicarbonate)	5
	Second coat (PEG 1500)	6
	Effervescent crumbling agent for the second coat (citric acid + sodium bicarbonate)	50
15	Third coat (PEG 1500)	2
	Crumbling agent for the third coat (sodium carbonate)	10

20        The foam control profile of these particles was assessed by the procedure quoted in Example 4. Foam heights after periods of 45 and 60 minutes were 9 and 30, respectively. There was no dispenser residue from powder incorporating these particles.

25

CLAIMS

1. Antifoam particles for incorporation into a detergent  
5 product comprising

a porous particulate organic carrier material,

a silicone antifoam with a viscosity of 10,000 cP or  
more absorbed onto the carrier material, and

a coating layer enclosing the carrier and absorbed  
10 silicone antifoam.

2. Antifoam particles according to claim 1 wherein the  
carrier has a Hildebrand solubility parameter of at least  
24MPa<sup>1/2</sup>.

15

3. Antifoam particles according to claim 1 or claim 2  
wherein the carrier does not melt below 100°C.

4. Antifoam particles according to claim 1 wherein the  
20 carrier material incorporates glucose residues.

5. Antifoam particles according to claim 1 wherein the  
carrier material is cellulosic.

25 6. Antifoam particles according to claim 5 wherein the  
carrier material is wood flour.

7. Antifoam particles according to claim 1 wherein the carrier material is proteinaceous.

8. Antifoam particles according to claim 7 wherein the carrier material is gelatine.

9. Antifoam particles according to any one of claims 1 to 8 wherein the organic carrier material has a mean molecular weight of at least 2,000.

10

10. Antifoam particles according to any one of claims 1 to 9 having two coating layers, one over the other.

11. Antifoam particles according to claim 10 wherein the second coating comprises polyethylene glycol of molecular weight greater than 4,000 and anhydrous acid dissolved therein.

12. Antifoam particles according to any one of claims 1 to 11 wherein a coating later incorporates particles of an acid, a carbonate and/or a bicarbonate to cause effervescence on contact with water.

13. A particulate detergent product comprising detergent active, detergency builder and antifoam particles according to any one of claims 1 to 12.

# INTERNATIONAL SEARCH REPORT

PCT/GB 92/01188

International Application

<b>I. CLASSIFICATION OF SUBJECT MATTER</b> (If several classification symbols apply, indicate all) <sup>6</sup>		
According to International Patent Classification (IPC) or to both National Classification and IPC Int.Cl. 5 C11D3/37;                      C11D17/00;                      B01D19/04		
<b>II. FIELDS SEARCHED</b>		
Minimum Documentation Searched <sup>7</sup>		
Classification System	Classification Symbols	
Int.Cl. 5	C11D ;                      B01D	
Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched <sup>8</sup>		
<b>III. DOCUMENTS CONSIDERED TO BE RELEVANT<sup>9</sup></b>		
Category <sup>10</sup>	Citation of Document, <sup>11</sup> with indication, where appropriate, of the relevant passages <sup>12</sup>	Relevant to Claim No. <sup>13</sup>
X	EP,A,0 206 522 (UNILEVER) 30 December 1986 see claims 1,2; examples ---	1,3-5,9, 13
X	EP,A,0 040 091 (UNILEVER) 18 November 1981 see claims 1,2,10 ---	1,4,10, 13
X	FR,A,2 462 184 (EURAND-FRANCE) 13 February 1981 see the whole document ---	1,3-5,7, 9,13
A	US,A,4 451 387 (L.H.T. TAI) 29 May 1984 see claim 1 -----	1,3-5,9, 13
<div style="display: flex; justify-content: space-between;"> <div style="width: 45%;"> <p><sup>10</sup> Special categories of cited documents :</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> </div> <div style="width: 45%;"> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.</p> <p>"&amp;" document member of the same patent family</p> </div> </div>		
<b>IV. CERTIFICATION</b>		
Date of the Actual Completion of the International Search  <div style="text-align: center; font-weight: bold;">25 NOVEMBER 1992</div>	Date of Mailing of this International Search Report  <div style="text-align: center; font-weight: bold;">- 4. 12. 92</div>	
International Searching Authority  <div style="text-align: center; font-weight: bold;">EUROPEAN PATENT OFFICE</div>	Signature of Authorized Officer  <div style="text-align: center; font-weight: bold;">GRITTERN A.G.</div>	

ANNEX TO THE INTERNATIONAL SEARCH REPORT  
ON INTERNATIONAL PATENT APPLICATION NO.

GB 9201188  
SA 61396

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report.  
The members are as contained in the European Patent Office EDP file on  
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FR-A-2462184	13-02-81	None	
US-A-4451387	29-05-84	None	

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For more details about this annex : see Official Journal of the European Patent Office, No. 12/82